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Abstract

THE CHEMISTRY OF THE TRIVALENT ACTINIDES IN AQUEOUS SOLUTIONS AND THEIR RECOVERY

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The irradiation of plutonium in a reactor, as fuel or target, eventually produces actinide elements, besides the fission products. The former can be irradiated in turn to yield still higher actinides, which have some practical uses - curium as a heat source in satellites, californium as a neutron source, and others. The recovery and purification of these materials necessitates a familiarity with their chemistry.

The transplutonium elements occur mainly in the trivalent state, and have chemical properties similar to those of the lanthanides. However, the chemistry of both groups in aqueous solutions useful for separation processes has only recently been studied in detail. Ion exchange and solvent extraction processes using acid phosphate esters, hydroxy-carboxylic acids and concentrated chloride and nitrate solutions play important roles in the separation of the actinides, mutually and from other elements.

A survey of the chemistry of the actinides in these and related media shows how the properties of these complex systems contribute to the separation and recovery processes.

The separation of actinides by elution with, e.g. alpha-hydroxyiso-butyric acid, from a cation exchanger, parallels the separation of the lanthanides. This process, indeed, was the only one capable of allowing the chemical identification of the heaviest actinides produced. The separation factors for neighboring elements are moderately high (1.6). These elements form complexes with up to four bidentate chelating ligands, and the anionic complexes formed are octo-coordinated. The relative stability of the actinide and lanthanide complexes with these and related ligands may

be correlated with properties such as the crystal ionic radii. Ligand field effects seem to be unimportant.

A competitive process for mutual separation of the actinides is their extraction (e.g. in reversed phase chromatography) by an acidic phosphate ester, such as di-(2-ethylhexyl) phosphate. The separation factors (2.5) are even larger than in the above process. The complexes formed generally have three dimeric ester ligands, but complications occur in certain systems. The synergistic action of reagents such as T.B.P. can enhance distribution coefficients and mutual separability. These actinide complexes have apparently coordination numbers of either six or eight.

The above processes cannot separate the actinides from the lanthanides present as fission products in process solutions. This can be accomplished by anion exchange or amine extraction from concentrated lithium chloride solutions at low acidity. This indicates that anionic complexes are formed, but spectrophotometric measurements in our laboratory on the lighter trivalent actinides, uranium to americium, show that only weak cationic complexes are active spectroscopically, as shown by the appearance of new U.V. peaks.

Good anion exchange separation of americium and curium may be obtained with lithium nitrate rather than chloride. The behaviour of the heavier actinides has also been compared in this laboratory with the unusual even-odd atomic number effect shown by the lanthanides, and some information on the electronic state of these ions has been obtained.

In conclusion, although some separation processes utilise the different oxidation states of the actinides to obtain efficient separation (e.g. of Am(VI) and Bk(IV)), the key to their recovery still lies in the knowledge of the behaviour of the trivalent state in aqueous solutions.